Monte Carlo simulation of ferroelectricity induced by collinear magnetic order in Ising spin chain

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To understand the collinear-magnetism-driven ferroelectricity in the frustrated Ising spin chain, the fascinating magnetoelectric behavior is investigated by using Monte Carlo simulation based on one dimensional elastic Ising model. Our simulation quantitatively reproduces the experimental results of the complicated electric and magnetic behaviors as functions of temperature observed in Ca₃CoMnO₆ compound [Phys. Rev. Lett. 100, 047601 (2008)]. Moreover, the short-ranged up-up-down-down magnetic ordering is confirmed to be the origin of electric polarization, and the curves of energy components dependent on temperature provide a reasonable explanation for the unconventional magnetoelectric phase transition revealed in the Ising chain magnet. © 2008 American Institute of Physics. [DOI: 10.1063/1.3009321]

I. INTRODUCTION

Due to the potential applications and fundamental academic curiosity, the investigation of multiferroic materials, especially magnetoelectric (ME) coupling compounds, has attracted considerable attention in recent years. In particular, the magnetism-driven ferroelectricity was discovered in many frustrated systems, which renewed the interest of investigation in this field. As revealed in these compounds, the strong coupling between the electric polarization and the magnetic ordering provides a possibility of simultaneously controlling magnetic and electric degrees of freedom. In order to achieve their potential applications, it is very essential to understand how these two degrees of freedom are coupled to each another at a microscopic level. Unfortunately the corresponding microscopic mechanism has not been unveiled until now.

The noncollinear magnetic phase, especially the spiral spin ordering, is a common way to magnetism-driven ferroelectricity. Microscopically, the ME mechanism of the spin current and the Dzyaloshinskii–Moriya interaction were proposed for these noncollinear magnets. Besides the noncollinear magnetism, other magnetic orderings are also possible routes toward ME coupling and ferroelectricity. Microscopically, the ME mechanism of the complicated electric and magnetic behaviors as functions of temperature observed in Ca₃CoMnO₆ compound [Phys. Rev. Lett. 100, 047601 (2008)]. Moreover, the short-ranged up-up-down-down magnetic ordering is confirmed to be the origin of electric polarization, and the curves of energy components dependent on temperature provide a reasonable explanation for the unconventional magnetoelectric phase transition revealed in the Ising chain magnet. © 2008 American Institute of Physics. [DOI: 10.1063/1.3009321]

II. THEORY AND MODELING

Ca₃CoMnO₆, belonging to the family of 1D spin-chain materials, can be regarded as a doped compound of Ca₃CoO₆, which represents one of the most frequently studied compounds due to its complex magnetic properties. With half of Co ions replaced by Mn ions, Ca₃CoMnO₆ consists of parallel 1D CoMnO₆ chains, aligned along the hexagonal c-axis and separated by Ca²⁺ ions. It forms a triangular lattice in the ab-plane. Each spin chain is composed of alternatively face-sharing CoO₆ trigonal prisms and MnO₆ octahedra along the c axis where the Co²⁺ ion is the low-spin and Mn³⁺ ion is the high-spin. Due to the much stronger intrachain interaction than the interchain one and the strong Ising-like anisotropy, this compound can be characterized by a 1D Ising model. Based on the former investigation, the ferromagnetic (FM) coupling (JFM>0) between each nearest-neighboring Mn–Co spin pair and the next-nearest-neighbor antiferromagnetic (AFM) interaction are considered in order to generate spin frustration and accordingly produce the up-up-down-down spin structure. Since the magnetic moment of Mn ion is about three times larger than that of Co, that is 1.93 μB and 0.66 μB for Mn and Co ions, respectively. The AFM coupling between each next-nearest-neighbor Mn–Mn pair should be stronger than that for Co–Co (JAFM<0). For simplicity, JAFM≈9 JAFCo is assumed. In addition, in the pure up-up-down-
down spin state the exchange striction has no effect on the next-nearest-neighboring spins, therefore the exchange striction is only considered for \( J_{FM} \) here. No matter what form of distance dependence for \( J_{FM} \) between the nearest-neighboring spins is, it can be expanded to the following linear approximation form:

\[
J_{FM}(r_{i,i+1}) = J_{FM0} \left( 1 + \eta \frac{r_{i,i+1} - r_0}{r_0} \right) = J_{FM0} \left[ 1 + \eta(d_{i+1} - d_i) \right],
\]

where \( J_{FM0} \) is defined as the bare FM spin-spin interaction, and \( \eta \) gives the strength of the coupling between the spins and the displacements. \( \eta < 0 \) reflects that the interaction gets stronger as the spins get closer to each other, and vice versa. \( r_0 \) is the original distance between two ions without the exchange striction, \( r_{i,i+1} \) is the distance between the \( i \)th ion, and the \((i+1)\)th ion under the exchange striction. \( d_i \) denotes the displacement of the \( i \)th ion normalized by \( r_0 \) and it bears a positive value when this \( i \)th ion is approaching the \((i+1)\)th one. According to Eq. (1), the change in \( J_{FM} \) is related to the change in the distance between the spins, therefore the relative movement of the ions is the key for the exchange striction. For simplicity, it is assumed that only Co ions move, namely, \( d_i \neq 0 \) for Co, but \( d_i = 0 \) for Mn case. The Hamiltonian of this 1D Ising model can be written as

\[
H = - \sum_{(i,j) \in Mn} J_{FM0} S_i S_j - \sum_{[i,k] \in Co} J_{FM0} S_i S_k - \sum_{[i,k] \in Co} J_{AFCo} S_i S_k - \sum_{[i,k] \in Mn} J_{AFCo} S_i S_k - \frac{1}{2} k \sum_i d_i^2.
\]

where \( S_i = \pm 1 \) represents the \( i \)th spin of the chain, \( \langle i,j \rangle \) denotes the summation over all the nearest-neighboring spin pairs, and \([i,j]\) signifies that over all the next-nearest-neighboring pairs, which is calculated for Mn and Co respectively. \( h \) is the external magnetic field applied along the direction of spin chain, \( g \) is the Lande factor, and \( \mu_B \) is the Bohr magnetron. \( E \) is the electric field also applied along the chain and \( q \) is the charge state of the moving ions, that is \( q = 2 \) for Co\(^{2+}\). The last term on the right of Eq. (2) is the elastic energy presented in the form of the harmonic potential, where \( k \) is the elastic constant with the value large enough to ensure the small values of the ionic displacements. For convenience, \( k_B \) is chosen to be unity, and the other parameters are scaled by the above assumption. The values of these parameters for the simulation are shown in Table I. Since the real values of these parameters are not available from experiments, they are chosen by the qualitative comparison between the simulated results and the experimental data.

III. RESULTS AND DISCUSSION

Our simulation results are presented on the left column of Fig. 1, and the corresponding experimental data from Choi...
Comparing with the experimental results on the right column of Fig. 1, data, which is presented in the following three aspects. First, our simulation result is qualitatively in good agreement with experimental results. It can be seen that our simulation promises to the exchange striction in an up-up-down-down ordering are formed, and then a macroscopic $P$ emerges. As illustrated in Fig. 2(a), the short-ranged feature of up-up-down-down ordering is also consistent with the neutron diffraction experiment. At low $T$, these polarized domains are frozen due to the spin frustration. However with $T$ increasing toward $T_p$, the frozen domains gradually melt and the displacements of ions cannot keep to the polarized direction anymore, as shown in Fig. 2(e). The counteraction between the polarized domains with two opposite directions leads to the sharp decrease in macroscopic polarization. Besides, these melting domains are sensitive to the electric field, namely, a small electric field may make these domains aligned along the same direction and consequently $P$ increases, which results in the peak of $\chi$. As $T$ is raised to $T_p$, the short-ranged up-up-down-down AFM state collapses, where $\chi$ shows a broad peak, and then $P$ fades away gradually. When $T$ above $T_p$, the ionic displacements show a disorder paraelectric character as presented in Fig. 2(f), which coincides with the linear behavior of the reciprocal of $\chi_e$ [Fig. 1(c)].

The temperature dependence of the electric and magnetic properties can be further understood by analyzing the energy of the system. In order to study this dependence, the main components of energy are listed in the following:

$$H_{FM} = -\sum_{(i,j)} J_{FM}(r_{ij}) S_i S_j,$$

$$H_{AF} = -\sum_{[i,k]} J_{AF_{Mn}} S_i S_k - \sum_{[i,k]} J_{AF_{Co}} S_i S_k,$$

$$H_M = -hg\mu_B \sum_i S_i,$$

$$H_{el} = \frac{1}{2}k \sum_i d_i^2.$$

Equations (5)–(8) respectively represent the FM energy between the nearest-neighbor spins, the AFM energy between the next-nearest-neighbor pairs, the magnetic energy, and the elastic energy induced by ionic movements. The temperature

**Fig. 2.** (Color online) (a) Partial snapshot of spins in a chain for $h=0$ and $T=1$, and (b) the corresponding snapshot for the displacement of ions, (c) enlarged view of spins extracted from the snapshot in (a) over eight ionic sites, and (d) enlarged view of the corresponding displacement extracted from the snapshot in (b). The sketches of these eight ions are presented on the top of (a). Partial displacement snapshots of the chain are plotted in (e) at $h=0$ and $T=2.8$, (f) at $h=0$ and $T=5.5$, and (g) at $h=4$ and $T=1$.
dependence of these energies at \( h=0 \) and \( h=4 \) are respectively shown on the left and right columns in Fig. 3. The competition of different energies induces the phase transition taking place at \( T_p \). In Figs. 3(a), 3(b), and 3(d), \( H_{FM}, H_{AFM}, \) and \( H_g \) all exhibit anomalies at \( T_p \). In particular, \( H_{FM} \) and \( H_d \) are minima, while \( H_{AF} \) attains maxima. It is implied that the up-up-down-down AFM state collapses and the exchange striction is the weakest at this temperature. Consequently the movements of ions are suppressed. In a macroscopic view, \( P \) disappears, and \( x \) presents a broad peak denoting the AFM transition. When the magnetic field of \( h=4 \) is applied along the chain, \( H_{FM} \) is lower but \( H_{AF} \) is higher than those with \( h=0 \) as shown in Figs. 3(e) and 3(f). It is indicated that \( h \) suppresses the up-up-down-down state and also the exchange striction [Fig. 3(h)]. Accordingly, the displacements of ions are also suppressed to a certain extent as demonstrated in Fig. 2(g). It is worthwhile to note that \( h \) results in the stepwise nature of \( H_M \) [Fig. 3(g)], which creates several inflexions of \( P(T) \) graphs under magnetic field. Moreover, \( P(T) \) curves of different \( h \) cross each other.

**IV. CONCLUSION**

In summary, the collinear-magnetism-driven ferroelectricity in a frustrated Ising spin chain with the competing nearest-neighbor FM and next-nearest-neighbor AFM couplings is investigated by using MC simulation. The simulation result is qualitatively consistent with the experimental results. The electric and magnetic properties obtained in our simulation present a clear scenario of the complicated ME behaviors observed in Ca\(_3\)CoMnO\(_6\). The snapshots of ionic spins and displacements confirm that the ferroelectricity in this compound is induced by a collinear magnetic ordering. Also the temperature dependence of different energy components is discussed to further understand the exotic ME transition. Although the real material is far more complicated than the present model, the simulated results are believed to cast some light on the understanding of the ferroelectricity driven by the collinear magnetic ordering in the frustrated system.

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